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(54) Flexible microporous rubber base articles and process for producing these

(57) The invention relates to microporous articles made of polymeric materials. Such articles may, in one example, be battery separators for electrical storage batteries.

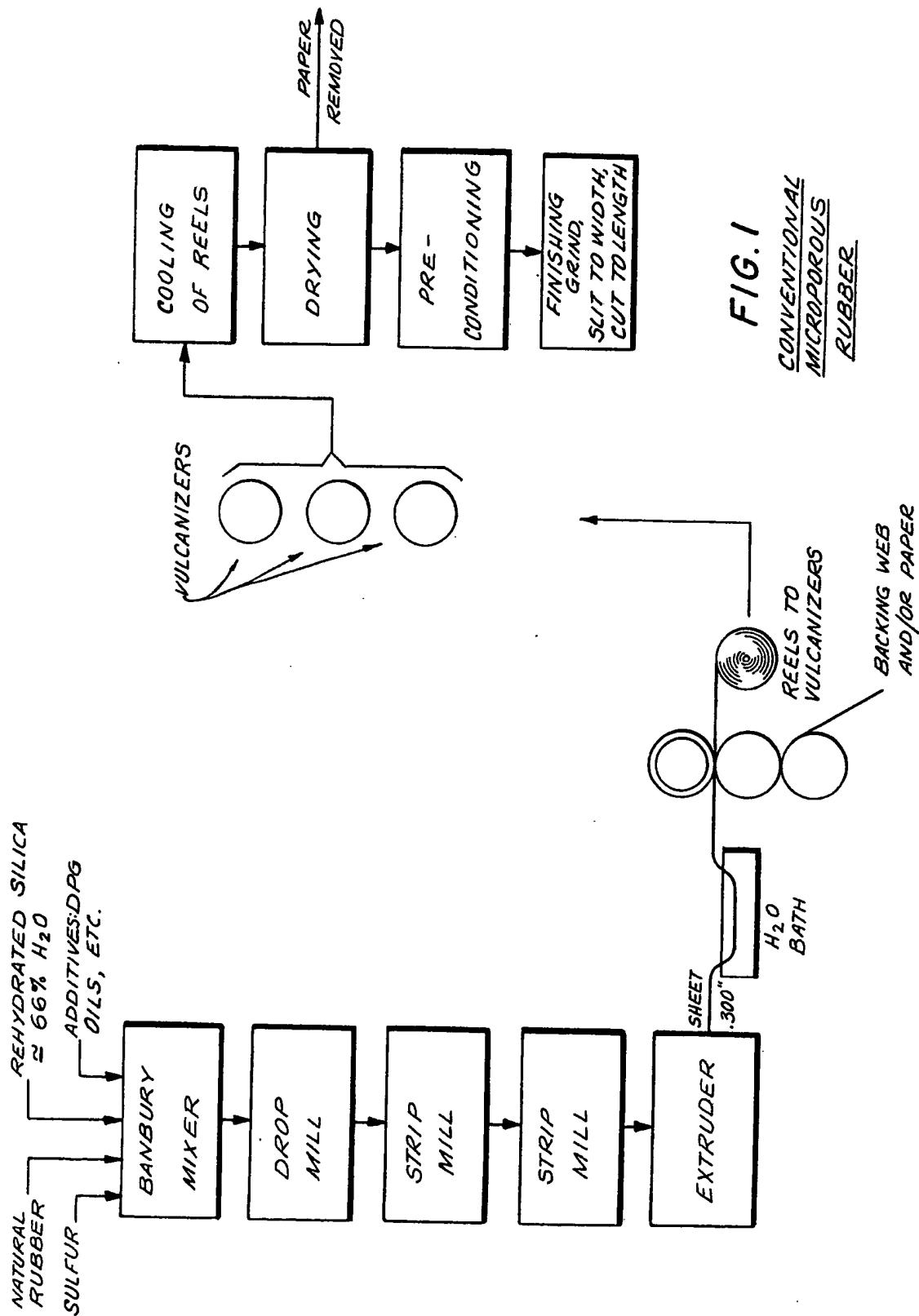
In one embodiment, the article comprises a microporous flexible

shape or sheet of a sulfur-free, cured polymeric material of a curable rubber an ethylene-propylene copolymer or mixtures of the curable rubber and ethylene-propylene copolymer. The article possesses an average pore size of less than 2 microns, a predetermined flexibility, and improved toughness, when compared to prior art sulfur cured articles. A continuous production of the cured rubber base material has been found to be especially advantageous.

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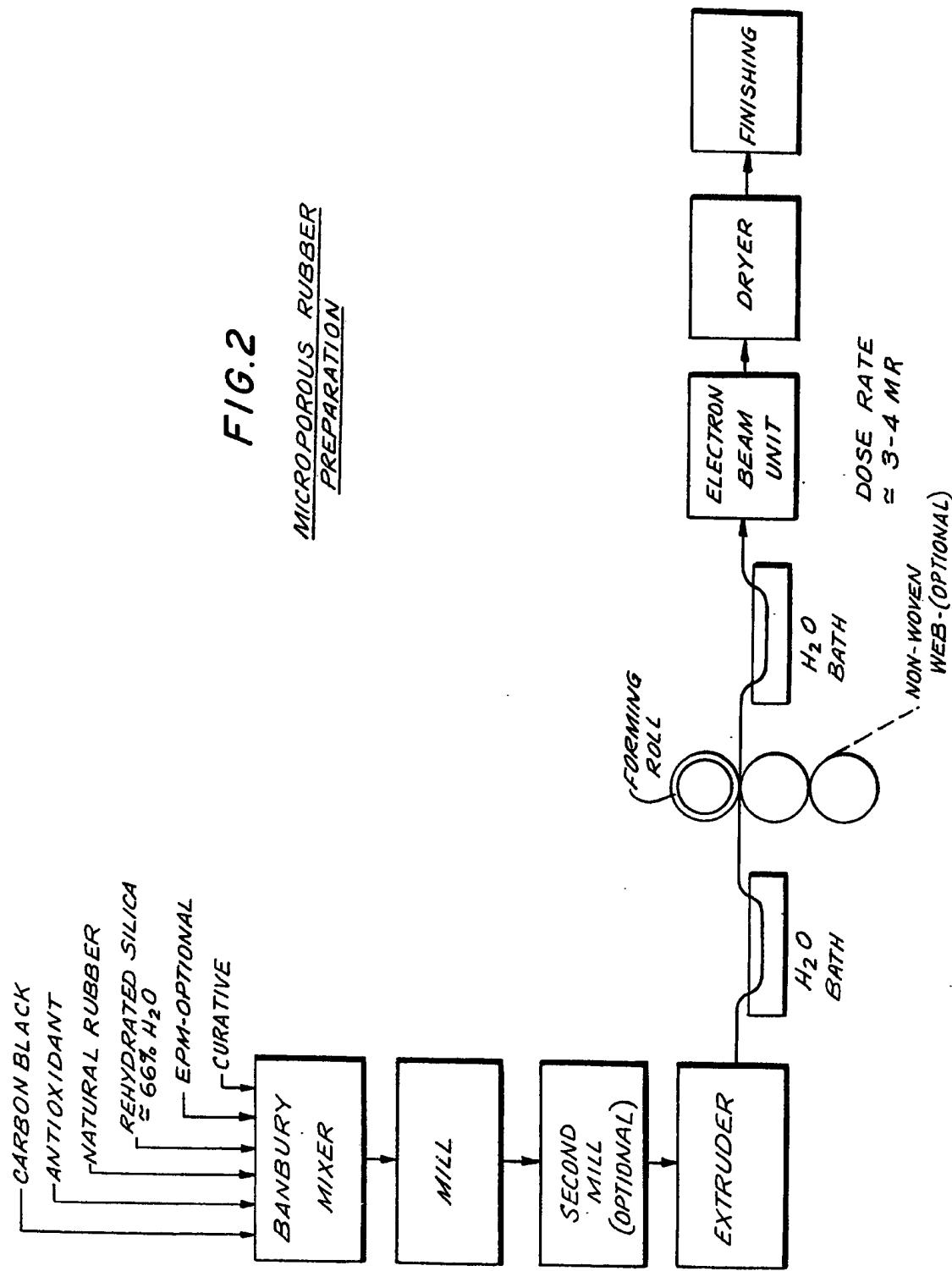
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SPECIFICATION**Flexible microporous rubber base articles and process for producing these**

This invention pertains to microporous articles made of polymeric materials; more particularly, this invention pertains to cured polymeric compositions wherein the average pore size is less than 2 and, more commonly, less than 1 micron and wherein the article can be tailor-made to be of varying degrees of flexibility ranging from completely drapable material to a relatively stiff material, yet non-brittle and tough having flexibility and toughness characteristics heretofore unknown in sulphur cured materials. A microporous sheet backed with a non-woven web is also disclosed having a number of properties heretofore unknown such as elongation greater than 25%, tensile strength up to 1000 psi and above, etc. This invention also pertains to a continuous process for producing cured polymeric compositions by electron beam irradiation at heretofore unknown low irradiation levels; the cured polymeric material deposited on a backed material may be made of thickness heretofore not possible.

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In commonly used electric storage batteries, such as the well known 12-volt battery employed in cars, it has been a desiratum to have a battery separator between the battery plates as thin as it is possible to obtain so as to have the lowest possible electrical resistance. At the same time, it has been sought to obtain a battery separator which is reasonably flexible and yet does not develop failure in use as brittle failure.

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Generally, a battery separator is needed as a spacer to prevent two plates from touching each other causing a short. At the same time, a separator shall not impede the electrolyte flow. Also, a fine pore size is desirable to prevent dendrite growth developing between adjacent plates. The result of dendrite growth is a battery "short". For one or more of the reasons given above, it has been necessary not only to increase the battery plate spacing, but also to use battery separators.

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Various other problems have also resulted from spalling of the battery plates associated with the use of antimony or calcium additives to the lead plates. Spalled deposits at the bottom of the battery have likewise caused shorts or premature failure of the battery. For this reason, it has been sought to have a battery which could be made in a manner whereby the battery separators could be festooned around the plates or made in a serpentine fashion thereby isolating one plate from the other.

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However, the prior art battery separators have been invariably rather stiff and inflexible; complex shapes could only be formed with great difficulty. In addition to the above problems, overvoltage caused at the electrodes, particularly at an anode, has required the well known addition of battery water.

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Only recently the overvoltage problem has been solved to a point such that maintenance-free batteries can be used with any degree of satisfaction. In no small part this has been a result of better plate or electrode materials or battery separators.

In the art of producing battery separators, commonly as a cheap and fairly short-lived separator, paper webs have been used. However, these possess disadvantages and instead of paper, better quality batteries have, as separators, cured natural rubber compositions. A common disadvantage inherent in the use of rubber or natural rubber based battery separators is that a sulfur cure process not only is capital intensive, being a batch process, but it is also labor and energy intensive. Sulfur curing of natural rubber microporous articles results in stiff and brittle products. Moreover, in order to maintain the porosity provided by rehydrated silica, a battery separator must be sulfur cured in a water filled autoclave. Repeated raising and lowering of temperature of large amounts of water is very energy consuming.

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Further, a sulfur cure process is capital intensive requiring compounding mixers, milling equipment, extruders, a battery of vulcanizers, etc.

45 In the curing of the rubber compositions, the cured articles are tested for cracking and brittleness. Unless very careful processing steps are followed in making sulfur cured separators, problems of brittle cracking often result. Dimensional tolerances are also difficult to maintain, for example, cured sheets from which battery separators are made require grinding.

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As a partial solution to the above problems associated with sulfur cured rubber products, phenolformaldehyde resin impregnated webs have been used as battery separators. The polyphenol resin is generally cured to a B stage and produces a stiff battery separator.

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Processing of phenols and formaldehyde, disposal of residues thereof, and shortcomings of the end product, such as large pore size and poor oxidation resistance, has thus far limited the use of the process as well as the article.

55 As another approach to solving the prior art problems, a polyvinyl chloride (PVC) impregnated wet has been proposed as a battery separator. However, production of these impregnated webs requires using solvent systems and solvent removal which contribute to unwanted disposal and contamination problems.

A PVC web also must be heat-embossed or hot-embossed to produce the necessary ribbing for allowing electrolyte flow and necessary strength.

60 As another battery separator, a melt blown polypropylene mat has been proposed. Moreover, the pore size of the mat has been excessive and unacceptable and electrical resistance characteristics have been hard to control.

These prior art efforts have required entirely new machinery and new processing techniques

obsoleting existing facilities associated with sulfur curing of natural rubber.

A number of microporous articles and techniques for producing these permeable, microporous products have been disclosed, such as in U. S. Patents 2,274,260, 2,329,322, 2,336,754, 2,686,142, 2,637,876, 3,298,869, 3,450,650, 3,773,540, 3,890,184, 3,900,341 and Canadian Patent 1,020,184

5 and reference is mentioned in these patents and further amplify the above description. 5
It has now been found that the microporous sheet material of predetermined, tailor-made flexibility, improved toughness, and elongation can be produced with assured microporosity and other properties which are better than the best heretofore known sulfur-cured rubber microporous article. A far-and-away greater flexibility of the new article has been accomplished without a sacrifice of the other 10 properties or performance of the article in use, such as a battery separator. The discovered material 10 ranges from flexible drapable sheets to stiff, tough, yet non-brITTLE boards. Hence, as one aspect of the invention, a battery separator has been disclosed which can now be readily shaped to any desired contour, can be made of various thicknesses, and can also be used in combination with a backing material. The newly discovered microporous material can be employed as microporous fibers, enzyme 15 carriers, diffusers, fabric materials, and possesses numerous advantages which will be further explained 15 herein.

As another aspect of the invention, a battery separator has been disclosed with a backing of heretofore unknown character possessing properties in combination such as low electrical resistance, reduced amount of microporous material (in combination with the backing), and improved tensile, tear, 20 toughness, elongation, and resistance to distortion. A superior combination has been discovered which 20 is a synergistically coating combination of the newly discovered microporous rubber base material and the flexible backing material.

Still further, a composition of matter suitable for producing these microporous articles has been disclosed. It is a curable composition. This curable composition has been found to be especially suitable 25 for electron beam curing. Moreover, the composition displays the superior properties when used with curatives heretofore unknown for that purpose, but curatives which are especially efficacious when subjected to electron beam irradiation. Synergistically coating polymeric compositions, each with the other, and with the curative(s) therefore, have reduced the irradiation levels to heretofore unknown levels. Whereas 25 typically for a cure, the prior art has suggested an irradiation dose for non-analogous products and 30 heavily sensitized compositions of curable natural rubber from 20 to 40 megarads of styrene-butadiene or nitrile-butadiene rubber from 14 to 15 megarads and EPDM (ethylene-propylene-diene) copolymer from 12 to 14 megarads, the present microporous precursor composition is effectively curable at an 30 irradiation level less than 6 megarads, preferably at about 3 to 4 megarads. Although curing at higher levels is possible, e.g., at 6 megarads and up, including up to 10, a number of properties suffer, such as 35 flexibility; hence, for economic and best product performance, irradiation is to be carried out at a dose rate of less than 6. A reduction in irradiation of such magnitude should be readily appreciated in an 35 industrial environment.

In accordance with the present invention, the precursor, noncured compositions, as well as the cured compositions are believed to be novel compositions of matter. 40
Still further, in accordance with the invention, a novel process has now been discovered for producing microporous articles, such as shapes or sheets of manufacture from curable rubbers, e.g., natural rubber, copolymers of ethylene and propylene, and mixtures of curable rubber and ethylene propylene rubbers (copolymers). The process has been found to be especially useful as it confers a number of advantages heretofore not possible to obtain when using the conventional technology such 45 as sulfur curing natural rubber to obtain microporous articles. Thus, the present process provides a continuous operation with reduced number of process steps and allowing the employment of some of the existing compounding machinery and apparatus for producing the microporous sheets or shapes. Still further, in accordance with the present process, the steps which have been found necessary in the prior art processes and most objectionable from the standpoint of environmental problems, disposal of 50 by-products, and energy requirements have now been eliminated. 50

As a further advantage of the present process, a very thin, flexible microporous article is produced which, in turn, permits a thin or thinner layer of the microporous polymer material to be combined with an appropriate backing material. When practicing the present process, an article can be produced without fear of distortion, handling problems, and material failure, such as brittle failure. 55
In accordance with the present invention, tailor-made articles of great flexibility can be produced resulting in the elimination of solvent system and elimination of heating and cooling of large amounts of water as well as elimination of batch processing operations.

The present process advantages reside in the discovery of the steps leading to the flexible material which comprise the proper compounding of the coating combination of curable rubber, e.g., natural 60 rubber, ethylene propylene rubber (copolymer), or mixtures of same with an especially suitable curative therefor properly proportioned (in combination with the polymeric material) and the above cured with rehydrated silica in the curing step. While it can be appreciated that curing at higher levels is possible, such as up to 8 or even 10 megarads, a number of disadvantages are evident, e.g., economic and safety factors, deteriorating properties, etc., hence, the preferred range is 4 megarads and less, i.e., amount 65 sufficient to cure the desired composition within a reasonable time. 65

In curing of the polymeric materials employed herein in admixture with the curative, the added rehydrated silica material does not apparently affect the effectiveness of the irradiation, but has indeed contributed to a product which, such as when irradiated at preferred levels of 3 to 4 megarads, confer properties on the end product such as on a battery separator heretofore not achievable.

- 5 The precise description of these compositions will be given below. In general terms, the curable composition consists of a curable rubber, e.g., natural rubber, polyisoprene, and various variants thereof, styrene-butadiene rubber, nitrile-butadiene rubber, or mixtures thereof; these may be used by themselves, but with considerably greater advantage when used in combination with ethylene-propylene monomer (rubber) (the last can also be used as the curable composition by itself) and as a 5
10 curative for the above, a polyol diacrylate, a polyol triacrylate, a polyol tetraacrylate, a polyol dimethacrylate, a polyol trimethacrylate, a polyol tetramethacrylate, or mixtures thereof. An illustrative, 10
15 advantageous curative is trimethylol propane trimethacrylate. It is postulated that upon curing, the curative contributes significantly to the end product performance.

- The invention will now be described by reference to the accompanying drawings wherein:
15 Figure 1 is a schematic diagram illustrating the essential steps in a conventional process for producing microporous articles by sulfur curing of a suitable rubber composition; and

- Figure 2 is a schematic illustration of the herein disclosed process.
By referring to the drawings herein, Figure 1 shows a conventional process wherein in a Banbury mixer the compounding of natural rubber, the sulfur curative, rehydrated silica, and suitable processing 20 additives, such as diphenyl guanadine mixing aid, oil, etc. are added. The sequence or order for the addition of these are varied, but generally, the curative and silica are added last. The mixture is mixed until a suitable drop (discharge) temperature has been reached. Thereafter, the discharged mixture is further processed such as on a two-roll drop mill until again the desired temperature for the mixing is achieved. From this mill, a suitable strip is formed in a strip mill (often requiring milling on an additional 25
25 strip mill for further processing thereof).

- From the strip mill, the compounded, curable mixture goes to an extruder wherein a sheet such as of .300 inches thick is being extruded and is thereafter introduced into a water bath. Subsequently, a support web is added to the formed microporous article. A support web is needed so as not to distort the rubber upon vulcanization. As a support web, paper is conventionally used. After forming a roll of the 30
30 extruded sheet of appropriate size, e.g., in diameter, the roll is ready for curing.

- Each wound up reel is then transferred to a vulcanizer wherein water at an appropriate temperature is raised to achieve the cure at about 350°F.

- The temperature is generally brought up at a steady rate of 40°F/min. under air pressure so as not to distort the sheet.

- 35 As soon as the microporous article is vulcanized, it is then cooled and discharged. So as not to again introduce distortion, cooling of the article is carefully conducted under pressure. Thereafter, drying of the cured article is carried out again in a batchwise manner in an appropriate dryer. In preconditioning the support web is removed from the cured and dried sheet.

- Inasmuch as in curing there is some distortion observed and inasmuch as it requires processing so 40
40 as to remove the unwanted distortion, each of the sulfur cured articles must be ground to obtain the desired contour. That is, proper dimensions and contours are obtained such as final thickness and ribbing for a battery separator. Thereafter, the article is slit to width and cut to length for packaging and sent to a manufacturer.

- In referring to Figure 2, it should be noted that the mixing of the components while indicated to be 45 simultaneously actually follows the procedure described below. For preparation of the master batch and compounding of the polymeric material, a more detailed description will be given. The present description will serve to illustrate the advantages of the present process and the steps in the process as shown in Figure 2.

- As the process provides the most benefits when carried on continuously, the emphasis will be on 50
50 the continuous aspects of the operation. In a suitably sized Banbury mixer or suitably sized series of mixers, the compositions disclosed herein are mixed. A next batch can be milled in time sufficient so that a two-roll mill can be at all times kept operating to feed ultimately to the extruder the mixed and compounded composition so as to maintain a continuous operation. Thus, Banbury mixers, the two-roll mills, and the extruder(s) are operated such that at all times a continuous supply is provided to the 55
55 extruder(s). The extruded sheet coming from an extruder is introduced in a water bath so as to maintain the rehydration level of silica and as shown in Figure 2. Again, if rehydration level can be appropriately controlled, the water bath may be optional. However, appropriate control of the amount of water in the mixture must be observed.

- A suitable forming roll having the desired ribs or other configuration can be used to shape the 60
60 article coming from the extruder and water baths. Advantageously shaping of the sheet can be at an elevated temperature such as 110°F to 140°F. After shaping, the continuously moving sheet is introduced into a water bath (optional) and therefrom into an electron beam unit which cures the composition at the indicated typical dose rate of 3 to 4 megarads.

- From the electron beam unit, the cured sheet is then introduced into a dryer wherein the water of 65
65 hydration is removed from silica and the microporosity thereby obtained. From the dryer, the sheet can

then go to a finishing operation wherein the material is slit to width, cut to length, as well as packaged in the conventional manner.

Hence, as one aspect of the invention, a battery separator can now be readily produced according to the novel process and when so produced, the separator can be shaped to any desired contour and

5 can be made of various thicknesses, including thicknesses heretofore unknown for rubber separators. These separators can also be made in combination with a backing material of thicknesses heretofore unknown for rubber separators. According to the present process, a very low resistance sheet is obtained of reduced thickness of the microporous material, improved tensile, tear, toughness, and resistance to distortion.

10 A superior product has also been produced by the present process as a coacting combination of the curable microporous rubber base material and a flexible backing material.

In the essential aspect, the process for producing the curable composition, the microporous material or any shape, e.g., a sheet, is best described by the following general example.

15 GENERAL EXAMPLE 15

A. Rehydration of Silica

The moisture content of the silica is determined first and then a correction is allowed for it before rehydration. Rehydration levels of 66.5% or 69.0% are typically employed but can range from 65 to 70%. One thousand grams (1000 g) of silica are introduced into a blender and the corrected amount of 20 water is pumped in at a rate of 800 to 900 cc/min. The pumping time of water should be fairly short of the order of few minutes as otherwise the blend gets too wet. After finishing the rehydration cycle, the blend is discharged and its moisture preserved. The blend should be in a powdered, friable form.

B. Masterbatch Procedure

The masterbatch preparation is desirable for obtaining a uniform mix of the curable composition, 25 In this example, ethylene-propylene copolymer (EPM) and/or natural rubber. Accordingly, the masterbatch consists of natural rubber, EPM, UV stabilizer, and carbon black. A required amount of EPM and natural rubber grind (about 1000 g as an illustration) are placed into a Banbury mixer and mixed for about 3—4 min. (at the second gear speed) until the temperature rises to 250°F. Then the UV stabilizer and/or carbon black (acting also as a UV stabilizer) are (is) added and the batch is dropped (discharged) 30 at 275°F. Total time is about 5 min. During this operation, a small amount of warm water (at about 150°F) is going through the rotors and body of the Banbury mixer to provide for temperature control. The total time required to make the masterbatch should be about 5 minutes. The masterbatch coming out of the Banbury mixer is placed on the two-roll mill (cold) and is sheeted out.

C. Compounding Procedure

35 A required amount of masterbatch (250—300 g) is milled on a two-roll cold mill until it became smooth (5 mins.) and then placed in the Banbury mixer with diphenyl guanidine (DPG)—as a mixing aid. The Banbury body temperature is 140°F with no heat or cooling water circulated to the rotor. The Banbury mixing speed is at its "slow" speed and when the temperature reaches 150°F, one-half of the required amount of rehydrated silica and a curative, e.g., trimethylol propane trimethacrylate (TMPTM) 40 are added. The composition is mixed until it again reaches 150°F and then the result of the rehydrated silica is added and is allowed to mix until it again reaches 150—160°F. The composition is then dropped. A very uniform mix is obtained and the total Banbury mixing time is about 8 minutes. Thereafter on a two-roll, this mixture is milled for about 7 to 8 minutes. Both mill roll temperatures are 140°F. The milled sheet is then cut into small pieces and soaked in hot water for 30 to 45 seconds at 45 50—85°C and is then calandered for contours and/or optionally a backing added thereto such as paper or heat-bonded polyester mat (The last is vastly more preferred as will be explained herein.) The temperature of both calander rolls is 130°F. The calandered sheet is cut into appropriate pieces, such as 15"×9" pieces, and is irradiated in an electron beam (EB) unit. After EB curing, these sheets are then dried at about 50° to 100°C to achieve the desired porosity.

50 D. Continuous Process 50

In a continuous process, instead as indicated in the foregoing part of the Example, after milling, a sheet is introduced into an extruder. A shape obtained from the extruder is immersed into a water bath at a temperature of 50—85°C so as not to lose any of the water of hydration associated with silica. Depending on the ability to control the amount of water in the shape, this water bath may or may not be 55 needed. A water bath at this juncture does provide a ready means for careful control of the composition. From this water bath, the extruded shape travels through a forming roll such as to produce a sheet of the desired surface characteristics for example, with ribs or other protuberances. If desired, a backing may be added to the polymeric material. Typically, an extruded sheet of the polymer, i.e., rubber or rubber and/or ethylene-propylene copolymer mixture is backed in the forming step.

From the forming roll, the sheet is again introduced into a water bath which is at a temperature about 25—85°F, and then into an electron beam irradiation unit wherein the sheet is irradiated at a dose rate desirably 4 megarads or less. Irradiation at higher energy levels than 6 megarads, and sometimes even at that level causes the composition to become unduly embrittled. From the irradiation unit, the continuously moving sheet travels to a dryer where the water of rehydration associated with silica is being removed so as to obtain the desired porosity and pore size. From there, the sheet travels to the finishing operations where it is being slit, cut, and packaged in appropriate containers for shipping to manufacturers utilizing the microporous articles such as for a conventional car battery.

Although the general example illustrates a small scale process, a scale-up of the process has followed the same steps as in the described examples and the continuous process illustration.

The description of the various components for the precursor composition is given below to illustrate the scope of the invention as well as to provide further elaboration on the embodiment discussed above.

As starting material, natural rubber is No. 1 smoked sheet possessing Mooney viscosities of about 25° to 30° at 175°F. On the basis of plasticity, the natural rubber should be between 14 to 18 (rheometer—50 scan). In place of natural rubber, synthetic polyisoprene, the various stereo specific variants and polymers thereof are also within the contemplation of the present invention as are mixtures of same with natural rubber.

Another polymer useful in the present process for the disclosed purposes is styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR), or mixtures of the above. It is, of course, to be understood that before curing, SBR and NBR are polymers which are not theremoset. All of the above polymers may be used in admixture with each other.

As a component, to impart the toughness, flexibility, and other desirable characteristics to the base composition, i.e., natural rubber, synthetic rubber, or mixtures of same, ethylene propylene rubber (copolymers) have provided unexpected and desired properties in the combination with rubber or even by itself. Although in the prior art, ethylene propylene copolymers are often either designated as ethylene propylene polymer or ethylene propylene monomer or ethylene propylene rubber, the more accurate description is a "copolymer consisting of ethylene and propylene" in various proportions typically ranging from 20 to 80% ethylene, balance propylene. (However, for sake of emphasizing the "rubber" aspect, it will be called ethylene-propylene rubber.)

A particularly desirable combination of the ethylene propylene rubber has been found to be one which has ethylene content of about 60% by weight in the copolymer, the polymer having a Mooney viscosity of about 30. This product is commercially available and known as EPCAR 306 and available from B. F. Goodrich & Co. Although other EPDM terpolymers have been investigated, the far-and-away preferred polymer is the ethylene propylene copolymer.

A more flexible product is obtained when rubber such as natural rubber is being used as the predominant or major component of the polymer in the compositions up to and including 100% of the curable material. However, greater rigidity and stiffness is obtained when higher amounts of ethylene propylene copolymer is used, e.g., in amounts from 20 to 30% or even 35%—more flexibility is obtained when the ethylene-propylene rubber is used in amounts as low as 3 to 5%. Approximately cured microporous articles have been obtained solely from natural rubber or solely from ethylene propylene rubber, mixtures of these, or mixtures of these with other curable rubbers previously mentioned cured with the following curative.

The curative for the above composition, either for the rubber, e.g., natural rubber or the ethylene propylene copolymer or mixtures thereof typically is an acrylate or a methacrylate of a polyol. The polyol may have a di, tri, or tetra functional polyol, the acrylate or methacrylate being formed with the hydroxyl groups of the polyol. The polyol may have from 3 up to 10 carbon atoms. Illustrative polyols from which the acrylates and methacrylates are formed are trimethylol propane, pentaerythritol, triethylene glycol, 1,6-hexane diol, etc. Mixtures of the acrylates and/or methacrylates of the above polyols are also included as curatives. Trimethylol propane trimethacrylate (TMPTM) has been found to be the species most suitable for the present purposes. Of the methacrylate or acrylate species, the methacrylate is preferred because of the vastly lesser problems of toxicity vis-a-vis the acrylate.

In the combination, typically the curative used is from 0.5 to 3 parts per weight per 100 parts of the curable rubber ethylene propylene copolymer, or the mixtures of same.

It has been found, however, that for certain articles of manufacture, such as battery separators, the amount of ethylene propylene copolymer in the mixture is desirably in the range from about 35 to 15%, most desirably, at about 20%. However, ratios of natural rubber to ethylene propylene to polymer such as of 70/10, 80/20, 75/25, 70/30, 60/40, 50/50, and up to 100 parts of ethylene propylene rubber have been evaluated. Appropriate microporous articles have been obtained solely from the curable rubber, e.g., natural rubber or solely from ethylene propylene copolymer cured with the above curative. The preferred combination of the two is given above. Various proportions of these components give various properties and thus allow to obtain the tailor-made characteristics.

In addition to the above, carbon black is being used as an additive which improves the stability (as a UV stabilizer) of the porous article by itself or in combination with an antioxidant (UV stabilizer).

Typically, carbon black is used from 0.5 to 3 parts per hundred (pph) of the polymer; and the

- stabilizer from 0.5 to 2 pph.
- 5 Of the various stabilizers, a butylated p-cresol dicyclopentadiene was found to be preferred. It is available as Wingstay—L from The Goodyear Tire & Rubber Co. Other stabilizers are such as styrenated diphenylamine, Wingstay 29 also available from The Goodyear Tire & Rubber Co. and polymerized 1,2 dihydro-2,2,4 trimethyl quinoline (FlecoAge from Monsanto Co.). 5
- 10 The silica powder is for introducing the porosity in the polymer. It is readily obtainable. One type is Hi—Sil 233 available from Pittsburgh Plate Glass Co. Generally, the surface area for silica should be greater than 50 m²/gr (B.E.T. procedure) and minimum oil absorption should be about 100 cc of oil or more per 100 gr of silica (ASTM method D—281—31). 10
- 15 Irradiation of the novel compositions is accomplished by an electron beam unit rated at 850 kw and 50 mA and available under the name of Dynamitron from Radiation Dynamics, Incorporated at Melville, New York. For purposes of the present invention, any electron beam unit capable of imparting a radiation level of 6 megarads is acceptable. Time of irradiation and power needed is a function of sheet or shape thickness. Hence, any reference herein to the irradiation level is to the same sheet or shape thickness. 15
- 20 In using a backing, it has been found that the open structure of a non-woven web is of an excessive "pore size" to be acceptable as a battery separator; however, the flexibility of a proper web to which a sheet of the microporous article can be securely attached could heretofore not have been utilized for want of a proper and flexible microporous sheet. Consequently, a flexible web and a fairly stiff brittle microporous sheet still had to be of considerable thickness and hence, are not used. With a 25 flexible microporous article and a flexible backing, the combination of the two allow the use of a thinner sheet of the microporous article, which is very advantageous not only because it provides less resistance in a battery, but also the more flexible sheet is less apt to be punctured, will not fail in flexing, and the flexible web, for example, adds virtually no resistance to the combination when used in an electrolyte. At the same time, the backing can be safely irradiated, provides a sufficient "body" to the 30 polymeric material and allows use of a polymeric material as thin as 5 to 8 mils. A thicker layer, for example, up to 25 mils, can still be used. Consequently, each use will dictate the appropriate thickness for the microporous layer with the backing material. 30
- 35 As a backing material, a polyester non-woven, heat-bonded (in distinction from an adhesive-bonded) web has been found to be especially desirable. An average fiber length in these webs is typically about .8 inches. These webs are available from duPont and Co. such as under the trademark Sontara 8000. 35
- 40 Properties of these webs are determined on basis of electrical resistance, tensile and tear strength. For battery separators, electrical resistance added as a result of the backing should be no greater than 1 mΩ in²/mil of thickness. Tensile strength should be about 100 lb/in², elongation about 40%. Tear strength for a base web of 1.2oz/yd, standard size should be measured by grab breaking strength (ASTM Method D—1682—65) and should be about 22 and up in machine direction and 13 and up in cross-direction. Generally, webs of a weight from .75 oz/yd (yard) to 2.2 oz/yd are available. 40
- 45 Typical ranges for properties of the above material are as follows:
- | | | | |
|--------------------------------|-------------------------------|-----------|----|
| Grab Breaking Strength (lbs.) | MD 20—30 | XD 12—18 | |
| Grab Breaking Strength (%) | MD 25—50 | XD 50—120 | 45 |
| Weight (oz./yd. ²) | 1.2—2.2 | | |
| Mullen Burst (lbs.) | 30—40 | | |
| Tongue Tear (lbs./in.) | about 2.1 MD and about 3.1 XD | | |
- 50 In the description herein, parts or percent are by weight, unless otherwise indicated. In further illustrating the present invention, specific examples are furnished in the Tables below. These examples show the various properties and characteristics of the composition in the various forms thereof. The examples are not to limit the invention. In the description herein, parts or percent are by weight unless otherwise indicated. 50

TABLE I
THE EFFECT OF VARIOUS STABILIZERS

	Formulation			
	A	B	C	D
Natural Rubber, g	80	80	80	80
EPM, g	20	20	20	20
Rehydrated Silica, g	360	360	360	360
Moisture in Silica, %	66.5	66.5	66.5	66.5
TMP™, g	3.0	3.0	3.0	3.0
Wingstay 29, g	-	1.0	-	-
Wingstay-L, g	1.0	-	1.5	2.0
Total Dose, MR	4	4	4	4
Dose Rate/pass, MR	2	2	2	2
Thickness, in.	0.018	0.015	0.023	0.020
Electrical Resistance, mΩ in. ²	56	50	72	60
Weight Loss in Chromic Acid, %	3.1	3.3	3.1	3.0
Comments before subjecting separator to fluorescent light	6.0	10.0	7.5	8.0
	flexible			
Comments after subjecting separator to fluorescent light for 7 days	No crack within 7 days, but cheap crack after 2 weeks	Very cheap crack	Flexible after 2 weeks, cheap crack after folding many times	Very good. No cracks after 1 month

TABLE II
THE EFFECT OF EPM BLENDING WITH NATURAL RUBBER AND
THE EFFECT OF VARIOUS TMPTM LEVELS

	E	F	G	H	I	J	K	L
Natural Rubber, g	100	90	80	75	80	80	80	-
EPM, g	-	10	20	25	20	20	20	100
Rehydrated Silica, g	360	360	360	360	360	360	360	360
Moisture In Silica, %	66.5	66.5	66.5	66.5	66.5	66.5	66.5	61.9
Dry Silica, g	-	-	-	-	-	-	-	26
TMPTM, g	3	3	3	3	1.0	1.5	2.0	1.5
Comments	good mix				slight mixing problem			
0 MR					Processed well			
Thickness, in.	0.017	0.018	0.016	0.015	0.016	0.015	0.019	0.029
Electrical Resistance, mΩ in. ²	54	54	48	57	50	47	57	58
mΩ in. ² /ml	3.2	3.0	3.0	3.8	3.1	3.1	3.0	2.0
Tensile Strength, psi	142	150	215	250	-	-	-	-
Elongation, %	14	13	10	5	-	-	-	-
Weight Loss in Chromic Acid, %					Not Recoverable			
Comments	very flexible				flexible, slightly stiffer			
					Cracked on one side			
					flexible			
					stiff, strong cracked when folded			

TABLE II (continued)

4 MFR		E	F	G	H	I	J	K	L
Thickness, in.	0.022	0.017	0.017	0.018	0.018	0.015	0.023	0.030	
Electrical Resistance, mΩ in. ²	55	50	46	60	50	40	60	60	
mΩ in. ² /mil	2.5	2.9	2.7	3.3	2.8	2.6	2.6	2.0	
Tensile Strength, psi	146	152	220	245	-	-	-	-	
Elongation, %	2	5	3	2	-	-	-	-	
Weight Loss in Chromic Acid, %	50.0	35.0	8.0	8.0	30.0	6.0	8.0	2.0	
Comments	Very flexible & Film	flexible	stiff	cracked on one side, stiff	flexible	stiff, tough, cracked			

TABLE III
FORMULATIONS STUDIED AT VARIOUS SILICA REHYDRATION LEVELS
AND RATIOS OF REHYDRATED SILICA/RUBBER

	1-A	1-B	Formulation	1-D	1-E
	1-A	1-B	1-C	1-D	1-E
Natural Rubber, g	80	80	80	80	80
EPM, g	2.0	20	20	20	20
Rehydrated Silica, g	360	433	480	433	468
Moisture of Rehydrated Silica, %	66.5	66.5	66.5	69.0	69.0
Wingstay-L, g	2	2	2	2	2
DPG, g	2	2	2	2	2
Carbon Black, g	0.5	0.5	0.5	0.5	0.5
TMPM, g	1.5	1.5	1.5	1.5	1.5
Theoretical Moisture, %	51.5	53.4	54.47	55.4	56.3
Plasticity	-	14	16	15	18
Time in Banbury, min.					
Drop Temperature of Banbury, °F.	8	8	8	8	8
Time on Mill (140° F.), min.	160-165	160-165	160-165	160-165	160-165
Temperature of Water Bath, °F.	7	7	7	7	7
Time in Water Bath, secs.	185	185	185	185	185
Temperature of Calender, °F.	40	40	40	40	40
	130	130	130	130	130

TABLE IIIA
PHYSICAL AND ELECTRICAL PROPERTIES OF FORMULATIONS WITH VARIOUS SILICA
REHYDRATION LEVELS AND RATIOS OF REHYDRATED SILICA/RUBBER

	0 MR	Formulations						1-E(B)
		1-A	1-A(B)*	1-B	1-B(B)	1-C	1-C(B)	
Thickness, in.	0.016	0.025	0.016	0.022	0.015	0.021	0.015	0.018
Electrical Resistance, mΩ in. ² /mil	46	54	39	32	30	34	36	36
mΩ in. ² /mil	2.9	2.2	2.4	1.5	2.0	1.6	1.8	1.7
Tensile Strength, psi	215	890	265	804	269	870	266	230
Elongation, %	10.0	35.0	6.8	37.3	6.0	42.0	18.0	1030
Pounds to Break	-	-	1.9	9.0	1.6	9.5	1.8	36.0
Weight Loss in Chromic Acid, %	-	-	47	63	Not Recoverable	68	47	10.6
Total Porosity, cc/g	-	-	-	-	0.498	-	62	60
Median Pore Diameter, μ	-	-	49.0	-	0.059	-	-	-
Moisture %	48.0	very flexible	-	-	50.0	-	-	-
Comments					flexible	51.0	55	51.9
 4 MR								
Thickness, in.	0.017	0.025	0.015	0.021	0.015	0.015	0.020	0.021
Electrical Resistance, mΩ in. ² /mil	44	46	30	32	30	31	30	38
mΩ in. ² /mil	2.6	1.8	2.0	1.5	2.0	1.5	1.5	1.8
Tensile Strength, psi	210	849	211	1190	247	1142	213	940
Elongation, %	4.0	30.0	1.0	35.0	1.0	34.5	1.0	243
Pounds to Break	-	-	1.5	10.6	1.9	11.5	1.5	1022
Weight Loss in Chromic Acid, %	8.0	5.3	8.0	6.0	8.0	5.0	9.0	28.0
Alcohol Porosity, %	-	-	47.0	61.0	61.0	66.0	48.0	2.0
Total Porosity, cc/g	-	-	0.513	0.894	0.533	-	33.0	1.0
Median Pore Diameter, η	-	-	0.041	8.5	0.043	-	8.0	BP**
Moisture, %	48.0	-	-	48.0	-	51.0	50.0	10.9
Comments					flexible and stiff	-	66.0	10.0
(B) - Sontara Backed						-	50.0	BP
BP - Broken Pieces						-	66.0	-
						-	53.0	-

In following the general example above, a composition was prepared consisting essentially of natural rubber—254 grams, TMPTM—7.6 grams, Hi-Sil—472 grams, water—875 grams. A cured product obtained from the above composition has a resistance of $1.3 \text{ m}\Omega \text{ in}^2/\text{mil}$ and $33 \text{ m}\Omega \text{ in}^2$. The above illustrates the relative ratios of silica to rubber and the reduced resistance, but flexibility is also reduced.

Another composition was obtained by following the general example; the constituents of the same were as follows: 88.2 lbs. of 80% natural rubber; 15% EPCAR 306; 5% Pliolite S—6F (an 82.5%styrene, balance butadiene rubber (SBR) available from The Goodyear Tire & Rubber Co.); 139 lbs. Hi-Sil 233; 1.3 lbs. TMPTM; 1.7 lbs. DPG and 239.6 lbs. water. An electron beam cured article

prepared from the above composition is suitable for forming various shapes or configurations of the cured material because the cured composition lends itself to ultrasonic welding. Accordingly, battery separators can be made as an envelope for a battery plate. It is to be understood that prior to curing, styrene-butadiene rubber and nitrile-butadiene rubber (NBR) are actually non-crosslinked, i.e., not thermoset polymers.

In the above described examples, weight loss in chromic acid is a typical gross test to establish unsaturation in the polymeric composition as well as useful life; and acceptable weight loss in less than 35%; it also typifies completion of curing and process efficiency with respect to crosslinking.

Similarly, shelf-life or storage stability of the cured microporous article is indicative of product life and is approximated by exposure to fluorescent light; typically, the composition should be good for at least 14 days before it develops cracks and loses flexibility.

The various measures of toughness of the unbacked, cured material are: tensile strength which should be in the range from 200 to 400 psi, preferably 300 to 400 psi. (For backed material, elongation in percent may be 20 to 90%, preferably 40 to 60%, and tensile strength up to 1200 psi.) Hence, it is now possible to produce very flexible shapes, i.e., conformable shapes when using thin sheets capable of great elongation; thicker sheets give tough, yet stiff products. Flexibility (non-brittleness) is easily measured by the 180° bend test and the present compositions easily meet this objective.

Again, while these values are generally pertinent to establish chemically desirable compositions, these values likewise can be used to establish the process variables vis-a-vis a standard.

A convenient measure of acceptable porosity is alcohol porosity and should be from 45 to 75%. Other measures of porosity have been given in the examples above and correspondingly, comparably acceptable values can be obtained from the above, first given value.

The electrical resistance norms for the battery separator are easily achieved; typically for the present microporous article, a resistance of 1.0 to $2.5 \text{ m}\Omega \text{ in}^2/\text{mil}$ is acceptable.

As mentioned before, dimensional stability of the shape during processing is outstanding and careful conduct of the process eliminates grinding of the end product. These advantages for the unbacked and backed material show the various advantages of the present invention.

In use in a battery, the battery separator is tested by conventional tests known in the art, e.g., a "cold cranking" test and "J—240" test identified by SAE testing procedures.

When employing a web, the thickness of the battery separator may be as little as 5 to 8 mils although typically a thickness of the separator is about 12 to 20 mils (backed) and from 10 to 20 mils without backing. Again, in a battery separator, the effectiveness of the thinner polymeric material on the web in combination is measured by the above two tests which also characterize the results of the process.

CLAIMS

1. As an article of manufacture, a microporous, flexible shape of a sulfur-free, cured polymeric material of a pore size less than 2 microns and a predetermined flexibility of curable rubber, ethylene-propylene polymer, or mixtures thereof, and a polyol acrylate, methacrylate, or mixtures thereof as a precursor curative therefor.

2. As an article of manufacture, a microporous, flexible shape of a sulfur-free, cured polymeric material of a curable rubber, ethylene-propylene rubber, or mixtures thereof, and a polyol acrylate, methacrylate, or mixtures thereof as precursor curative of a pore size less than 2 microns and of a predetermined flexibility wherein the same has a backing material of an inert polymer, nonwoven heat-bonded fibrous polymer, said backing material having a shelf-life resistance to an electrolyte for electrical storage batteries of at least equivalent to said microporous article.

3. The article as defined in claim 1, wherein the polymeric microporous article is a sulfur-free, cross-linked composition of rubber.

4. The article as defined in claim 3, wherein the polymeric microporous article is a sulfur-free, cross-linked composition of natural rubber.

5. The article as defined in claim 1, wherein the curable rubber is natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, a polyisoprene or mixtures of same.

6. The article as defined in claim 2, wherein the curable rubber is natural rubber, styrene-butadiene rubber, nitrile-butadiene rubber, a polyisoprene or mixtures of same.

7. The article of manufacture as defined in claim 1, wherein the microporous polymeric article is a

- sulfur-free, cross-linked polymeric material of natural rubber, ethylene-propylene rubber, or mixtures thereof.
8. The article of manufacture as defined in claim 1, wherein the microporous polymeric article is a sulfur-free, cross-linked polymeric material of natural rubber and ethylene-propylene rubber in percent by weight of natural rubber to ethylene-propylene rubber from 95 to 75% natural rubber to 5 to 25% ethylene-propylene rubber. 5
9. The article of manufacture as defined in claim 2, wherein the microporous polymeric article is a sulfur-free, cross-linked polymeric material of natural rubber, or ethylene-propylene rubber or mixtures of same.
- 10 10. The article of manufacture as defined in claim 2, wherein the microporous polymeric article is a sulfur-free, cross-linked polymeric material of natural rubber, or ethylene-propylene rubber in percent by weight of natural rubber to ethylene-propylene rubber from 95 to 75% natural rubber to 5 to 25% ethylene propylene rubber. 10
11. The article of manufacture as defined in claim 1, wherein a curative for said polymeric material 15 is a polyol diacrylate, a polyol triacrylate, a polyol tetracrylate, a polyol dimethacrylate, a polyol trimethacrylate, a polyol tetramethacrylate, or mixtures of same. 15
12. The article of manufacture as defined in claim 11, wherein the polyol is a trimethylol propane, pentaerythritol, triethylene glycol or 1,6-hexane diol.
13. The article of manufacture as defined in claim 11, wherein the polyol is a trimethylol propane. 20 14. The article of manufacture as defined in claim 2, wherein a curative for said polymeric material is a polyol diacrylate, a polyol triacrylate, a polyol tetracrylate, a polyol dimethacrylate, a polyol trimethacrylate, a polyol tetramethacrylate, or mixtures of same. 20
15. The article of manufacture as defined in claim 14, wherein the polyol is a trimethylol propane, pentaerythritol, triethylene glycol, or 1-6-hexane diol.
- 25 16. The article of manufacture as defined in claim 14, wherein the polyol is trimethylol propane. 25
17. As an article of manufacture, a battery separator for an electrical storage battery of a microporous, cured, flexible polymeric material of a rubber, an ethylene-propylene rubber or mixtures of same having a 180° bend flexibility, and a pore size of less than 1 micron.
18. The battery separator as defined in claim 17, wherein the same is of a cured polymeric 30 material of natural rubber and ethylene-propylene rubber. 30
19. The battery separator as defined in claim 17, wherein the polymeric material is of a cured natural rubber and an ethylene-propylene rubber in weight percent ranging from 75 to 95% natural rubber.
20. The battery separator as defined in claim 17, wherein the polymeric material is 80% by weight 35 natural rubber, 20% by weight ethylene-propylene rubber of about 60% ethylene monomer in said copolymer by weight. 35
21. The battery separator as defined in claim 17, wherein the microporous polymeric material further contains carbon black.
22. As an article of manufacture, a flexible, microporous battery separator of a sulfur-free, cured 40 polymeric material of a pore size of less than 1 micron, a 180° bend test flexibility, and an electrical resistance in an electrolyte solution for an electric storage battery of less than 3.5 mΩ in.²/mil. 40
23. The article of manufacture as defined in claim 17, wherein the same has a backing of a polymer fibrous material of heat-bondable fibers having at least an equivalent resistance to an electrolyte for an electric storage batery to said polymer material.
- 45 24. The article of manufacture as defined in claim 22, wherein the backing material is a non-woven, fibrous polymeric material of a polyester. 45
25. A curable, rubber composition for microporous shapes comprising as a curable material, a curable rubber ethylene-propylene rubber, or mixtures of same, and, as a curative therefor, a methacrylate or acrylate of a polyol, and rehydrated silica of 50 to 70% hydration as a micropore former 50 therefor.
26. The curable rubber composition as defined in claim 25, wherein the same comprises 80% by weight natural rubber, 30% by weight ethylene-propylene rubber having 60% by weight of ethylene as copolymer thereof, as a curative therefore trimethylol propane trimethacrylate and rehydrated silica of a 60 to 70% hydration, carbon black and a stabilizer therefore, said curable composition being curable via electron beam irradiation at less than 6 megarads. 55
27. The curable composition as defined in claim 25, wherein the same comprises 80% by weight natural rubber, 15% by weight ethylene-propylene rubber, and 5% by weight styrene-butadiene rubber, as a curative therefore trimethylolpropane trimethacrylate and rehydrated silica of a 60 to 70% hydration, carbon black and a stabilizer therefor, said curable rubber composition being curable via electron beam irradiation at less than 6 megarads.
- 60 28. In a curable polymeric material of natural rubber, ethylene-propylene copolymer or mixtures of same, the improved combination for curing of same, which comprises a polyol methacrylate or a polyol acrylate as a curative for said polymeric material for electron beam irradiation.
29. In a process for producing microporous polymeric material, the improvement comprising: 65 compounding a sulfur free curable composition of a curable rubber, ethylene and propylene

- rubber, or a mixture of same with a curative for curing the composition by electron beam irradiation, said curative therefor being an ethylenically unsaturated curing agent, and rehydrated silica; continuously forming a shape or said composition; and continuously curing said formed shape by irradiation at an irradiation level of less than 10 5 megarads.
30. The process as defined in claim 29, wherein curing is at an irradiation level of less than 8 megarads. 5
31. In a process for producing microporous polymeric material, the improvement comprising: compounding a sulfur free curable composition of a curable rubber, a copolymer of ethylene and 10 propylene, or mixtures of same with a curative for curing the composition by electron beam irradiation and rehydrated silica; continuously forming a shape of said composition; continuously curing said formed shape by irradiation at an irradiation level of less than 8 15 megarads; and recovering said cured product.
32. The process as defined in claim 29, wherein curing is at an irradiation level of less than 6 megarads. 15
33. The process as defined in claim 29, wherein the curable rubber composition is natural rubber, a polyisoprene, styrene-butadiene rubber, nitrile-butadiene rubber, or mixtures of same.
34. The process as defined in claim 29, wherein the curable rubber composition is natural rubber. 20
35. The process as defined in claim 29, wherein the curable rubber composition is natural rubber and styrene-butadiene rubber mixture. 20
36. The process as defined in claim 29, wherein the curable composition is an ethylene and propylene rubber.
37. The process as defined in claim 29, wherein the curable composition is an admixture of natural 25 rubber and an ethylene and propylene rubber. 25
38. The process as defined in claim 37, wherein an admixture of rubber and a copolymer of ethylene and propylene is from 65 to 95% by weight natural rubber and balance ethylene and propylene rubber.
39. The process as defined in claim 38, wherein in the admixture, rubber is 80% by weight. 30
40. The process as defined in claim 37, wherein the ethylene and propylene rubber has a Mooney viscosity of about 30.
41. The process as defined in claim 29, wherein during the said continuous forming of said shape the curable composition is extruded.
42. The process as defined in claim 29, wherein during the said continuous forming of said shape 35 the curable composition is extruded and in shaping to final form, backed with a sheet of an inert polymer, non-woven, heat-bonded web.
43. The process as defined in claim 31, wherein said curative is a polyol diacrylate, a polyol triacrylate, a polyol tetraacrylate, a polyol dimethacrylate, a polyol trimethacrylate, a polyol tetramethacrylate or mixtures thereof.
44. The process as defined in claim 43, wherein the curative is a polyol acrylate or methacrylate and said polyol is trimethylol propane, pentaerythritol, triethylene glycol, 1,6-hexane diol or mixtures of these acrylates, methacrylates or both methacrylates with acrylates. 40
45. The process as defined in claim 29, wherein the formed shape is electron beam irradiated within an irradiation dose of 4 and less than 4 megarads.
46. The process as defined in claim 29, wherein the formed shape is a battery separator in a form used in an electric storage battery. 45
47. The process as defined in claim 46, wherein the formed shape of said battery separator is electron beam irradiated and the recovered product is of a predetermined flexibility.
48. The process as defined in claim 47, wherein said battery separator is backed with a non-woven, inert, heat-bonded polymeric material of a polyester. 50
49. The process as defined in claim 29, wherein the sulfur free curable composition comprises 80% by weight natural rubber, 20% by weight copolymer of ethylene and propylene rubber having 60% by weight of ethylene as copolymer thereof, as a curative therefor trimethylolpropane trimethacrylate and rehydrated silica of 60 to 70% hydration, carbon black and a stabilizer therefor, said curable 55 composition being curable via electron beam irradiation of less than 6 megarads.
50. The process as defined in claim 21, wherein the curable composition is cured of an irradiation level of 3 to 4 megarads.
51. In a process for producing microporous polymeric material, the improvement comprising: compounding a sulfur free curable composition comprising of a curable rubber, an ethylene- 60 propylene rubber or mixtures of same with
- a) a curative for curing the same by electron beam irradiation, said curative being an acrylate or methacrylate of a di, tri, or tetra functional polyol or a mixture thereof, and
 - b) rehydrated silica;
- 65 maintaining a predetermined moisture content in said curable composition during processing of same while forming a shape of said composition; and 60

- curing said formed shape by irradiation at an irradiation level of less than 8 megarads.
52. Processes for producing articles, materials or compositions substantially as herein described.
53. Articles, materials or compositions produced by the method claimed in any of claims 29 to 52.
54. Articles, materials or compositions substantially as herein described.

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